PREPARATION OF NiO CATALYST ON FeCrAl SUBSTRATE USING VARIOUS TECHNIQUES AT HIGHER OXIDATION PROCESS

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ABSTRACT

The cheap nickel oxide (NiO) is a potential catalyst candidate to replace the expensive available platinum group metals (PGM). However, the current methods to adhere the NiO powder on the metallic substrates are complicated. Therefore, this work explored the development of nickel oxide using nickel (Ni) on FeCrAl substrate through the combination of nickel electroplating and oxidation process for catalytic converter application. The approach was started with assessment of various nickel electroplating process based on the weight gain during oxidation. Then, the next experiment used the best process in which the pre-treatment using the solution of SiC and/or Al_2O_3 in methanol. The specimens then were carried out to short term oxidation process using thermo gravimetric analysis (TGA) at 1000 ^{o}C. Meanwhile, the long term oxidation process was conducted using an automatic furnace at 900, 1000 and 1100 ^{o}C. The atomic force microscopy (AFM) was used for surface analysis in nanometer range scale. Meanwhile, roughness test was used for roughness measurement analysis in micrometer range scale. The scanning electron microscope (SEM) attached with energy dispersive X-ray (EDX) were used for surface and cross section morphology analysis. The specimen of FeCrAl treated using ultrasonic prior to nickel electroplating showed the lowest weight gain during oxidation. The surface area of specimens increased after ultrasonic treatment. The electroplating process improved the high temperature oxidation resistance. In short term oxidation process indicated that the ultrasonic with SiC provided the lower parabolic rate constant (k_p) and the Al_2O_3 and NiO layers were also occurred. The Ni layer was totally disappeared and converted to NiO layer on FeCrAl surface after long term oxidation process. From this work, the ultrasonic treatment prior to nickel electroplating was the best method to adhere NiO on FeCrAl substrate.

ABSTRAK

Nikel teroksida (NiO) yang murah adalah bahan yang berpotensi untuk menggantikan mangkin PGM yang ada. Namun begitu, kaedah semasa untuk proses perlekatan NiO pada substrat logam adalah rumit. Oleh sebab itu, kajian ini menerokai pengembangan *nickel oxide* menggunakan *nickel* (Ni) melalui kombinasi daripada *nickel electroplating* dan proses pengoksidaan. Pendekatan ini dimulakan dengan kajian pada pelbagai *nickel electroplating* process merujuk pada perubahan berat semasa pengoksidaan. Kemudian percubaan selanjutnya menggunakan proses yang terbaik iaitu rawatan awal menggunakan larutan SiC dan/atau Al_2O_3 dalam methanol. Specimen kemudian diperlakukan pada proses pengoksidaan jangkamasa pendek dengan menggunakan TGA pada 1000 ^oC. Sementara itu proses pengoksidaan jangkamasa panjang pada spesimen dilakukan dengan menggunakan *furnace* automatik di 900, 1000 dan 1100 ^oC. Spesimen dianalisis pada pembesaran oksida, morfologi permukaan dan penampang. AFM digunakan untuk analisis permukaan dalam skala nanometer. Sementara itu, alat ukur kekasaran digunakan untuk menganalisis pengukuran kekasaran dalam skala mikrometer. SEM disertakan dengan EDX digunakan untuk analisis permukaan dan morfologi lintang. Spesimen daripada FeCrAl dirawat menggunakan ultrasonic sebelum *nickel electroplating* menunjukkan perubahan berat terkecil selama masa pengoksidaan. Luas permukaan spesimen semakin meningkat selepas rawatan ultrasonik. Proses *electroplating* membaiki ketahanan pengoksidaan suhu tinggi. Pada proses pengoksidaan jangkamasa pendek menunjukkan bahawa ultrasonic dengan SiC menyediakan *parabolic rate constant* (k_p) yang lebih rendah dan lapisan Al_2O_3 dan NiO juga telah wujud. Lapisan Ni telah tiada dan mengalami perubahan menjadi lapisan NiO pada permukaan FeCrAl selepas proses pengoksidaan jangkamasa panjang. Daripada penyelidikan ini, rawatan ultrasonik sebelum proses *electroplating* merupakan kaedah terbaik untuk melekatkan NiO pada substrat FeCrAl.

CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS AND ABBREVIATIONS

Al	-	Aluminium
$Al(OH)_3$	-	Aluminium Hydroxide
Al_2O_3	-	Aluminium Oxide/ Alumina
$AlCl_3$	-	Aluminium Trichloride
AlOOH	-	Aluminium Oxide Hydroxide
AMO_3	-	3^{rd}-Transition Metal Perovskite
At%	-	Atomic Percentage
C_2H_6	-	Ethane
Ce	-	Cerium
CeO_2	-	Ceria
CH_4	-	Methane
CO	-	Carbon Monoxide
CO_2	-	Carbon Dioxide
Cr	-	Chromium
Cr_2O_3	-	Chromia
Cu	-	Cuprum
Fe	-	Ferum/Iron
Fe_2O_3	-	Iron Oxide
FeCrAl	-	Ferro Chrom Aluminium
h	-	Hour
H_2	-	Hydrogen
H_2O	-	Water
H_3BO_3	-	Boric Acid
HC	-	Hydrocarbon
Hf	-	Hafnium
k_p	-	Kinetic Parabolic Rate
La	-	Lanthanum

Mg	-	Magnesium
Mn	-	Manganese
N_2	-	Nitrogen
Ni	-	Nickel
$Ni(NO_3)_2.xH_2O$	-	Nickel (II) Nitrite
$NiAl_2O_4$	-	Nickel Alumina
$NiCl_2.6H_2O$	-	Nickel Chloride
NiO	-	Nickel Oxide
$NiSO_4$	-	Nickel Sulphate
$[Ni(NH_2SO_3)_2.4H_2O)]$	-	Nickel Sulphamate
NO_x	-	Nitrogen Oxide
O_2	-	Oxygen
Pd	-	Palladium
Pt	-	Platinum
Rh	-	Rhodium
SiC	-	Silicone Carbide
SiO_2	-	Silicon Oxide
Ti	-	Titanium
TiO_2	-	Titanium Dioxide
WO_4	-	Tungsten Oxide
Wt%	-	Weight Percentage
Y	-	Yttrium
Y_2O_3	-	Yttria
Zr	-	Zirconium
γ	-	Gamma
μm	-	Micrometer
AFM		- Atomic Force Microscopy
ASTM		- American Society for Testing and Materials
BATAN		- Badan Tenaga Nuklir Nasional (National Nuclear Energy Agency of Indonesia)
BES		- Back Scattered Mode
dm		- Decimetre
EDX		- Energy Dispersive X-ray
HIWI		- Hot Incipient Wetness Impregnation

kHz	- Kilohertz
MA	- Mechanical Alloying
mg	- Milligram
MHz	- Megahertz
mm	- Millimetre
OSC	- Oxygen Storage Capacity
PGM	- Platinum Group of Metals
SEM	- Scanning Electron Microscopy
STEM	- Scanning Transmission Electron Microscope
TGA	- Thermo Gravimetric Analysis
TPR-MS	- Temperature-Programmed Reaction Mass Spectroscopy
TWC	- Three Way Catalyst
UTHM	- University Tun Hussein Onn Malaysia
XRD	- X Ray Diffraction

LIST OF APPENDICES

CHAPTER 1

INTRODUCTION

1.1 Research background

Four ASEAN countries namely Indonesia, Malaysia, Philippines, and Thailand are facing major air pollution problems due to rapid economic growth, urbanization and motorization. Mortality and respiratory diseases caused by air pollution are believed to be endemic in cities of these countries. Regulations and standards are the first requirement for reducing emissions from both fixed and mobile sources. In order to reduce vehicle emissions, governments of the four countries are making efforts to introduce vehicle emission regulations for new vehicles. The common target is the introduction of EURO 2 standard by 2008 and EURO 4 standard by 2012. In order to abide the EURO 2 standard level, it is necessary to install catalytic converters to meet the emission regulation level (CO, HC, NOx, etc.) (Hirota, 2009).

Sudrajad (2005) mentions that the technology of vehicle emission reduction can be categorized into two major parts, namely primary and secondary method. For the primary method, it depends on fuel, on air treatment, and on a combustion process. Meanwhile, the secondary method is the use of a catalytic converter in the exhaust system of vehicles.

Catalytic converter is a device incorporated into the exhaust system of an automobile that reduces the amount of nitrogen oxides, carbon monoxide, and un-reacted hydrocarbons in automotive emissions (Sebayang *et al*., 2006). A catalytic converter as shown in Figure 1.1 consists of an insulated chamber (casing) containing a porous bed (substrate and washcoat), coated with catalyst material in which the exhaust gas must pass through before being discharged into the air (Searles, 2002). The catalytic material is used as a trigger to reduce or oxidize

reaction of HC, CO and NO, to reduce the amount of harmful products, i.e. H_2O, CO_2, N_2 and O_2 (Sebayang *et al*., 2007)

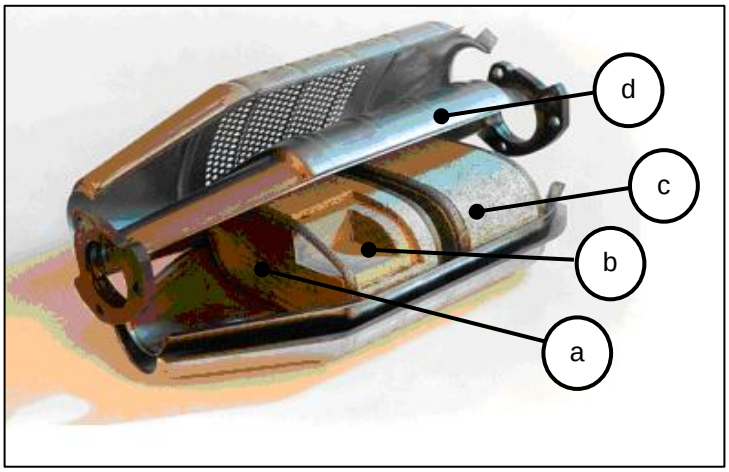


Figure 1.1: Catalytic converter components. a) substrate, b) washcoat, c) catalysts, d) casing (Searles, 2002)

There are many problems in the forming and manufacturing of the catalytic converter. Koltsakis & Stamatelos (1997) explains that the catalyst for catalytic converter is mostly related to the precious group of metals (PGM's) platinum, palladium, and rhodium. However, due to regulations, these materials are expensive and limited in developing countries, like in Malaysia. This is overcome by using nickel as a catalyst to replace the function of these precious groups of metals. Therefore, the utilization of nickel is investigated in this research.

The other challenge from the utilization of nickel as catalyst and FeCrAl as a substrate in catalytic converter manufacturing is the washcoat development. The washcoat is a kind of ceramic layer (oxide layer) which has specific surface area and acts as support for catalyst materials. The waschoat also acts as a barrier from high temperature corrosion (Cueff *et al.,* 2004).

This work investigates the new method to develop washcoat, to adhere nickel on the FeCrAl substrate, and to convert the nickel to be nickel oxide. The proposed method is coating technique using a combination of a nickel electroplating, ultrasonic treatment and oxidation process.

1.2 Problem statement

This is a great opportunity to utilize nickel oxide as a catalyst which is cheaper compared to the platinum group of metals (PGM's) in the catalytic converter application. The problems are how to coat the substrates with nickel oxide, how to create a large surface area, and how to develop washcoat as a catalyst carrier or high temperature barrier. The current methods which mostly used for adhering catalyst on the metallic substrate are a dip coating, co-precipitation, aluminizing and hydrothermal methods. However, these existing methods are mostly complicated, and usually employs alumina and catalyst material which in a form of powders. Therefore, this work explores a new one off method that combines various techniques, i.e. ultrasonic treatment, nickel electroplating, and oxidation process to develop nickel oxide on FeCrAl substrate.

1.3 Hypotheses

This study uses a combination of electroplating method, ultrasonic treatment and oxidation process. Therefore, the hypothesis in this study is as follows:

The FeCrAl coated with nickel is expected to will be obtained by nickel electroplating process. The better result is supposed will be obtained by modification of electroplating process, such as in the electrolyte solution compositions and stirring process. The coating process is believed will be stimulated by using ultrasonic treatment, which has cavitations phenomenon, i.e. cavity collapse near an extended solid surface becomes non-spherical, drives high speed jets of liquid into the surface, and creates shockwave damage to the surface. Finally, the alumina layer is expected to will be developed, and nickel will be converted to nickel oxide (NiO) by the oxidation process at an elevated temperature. Thus the application of nickel as a new catalyst in the catalytic converter will be achieved.

1.4 Research objectives

The objectives of this research are as follows:

(i) To develop NiO catalyst layer, Al_2O_3 layer, and high surface area on FeCrAl substrate.

(ii) To investigate the effect of ultrasonic treatment and nickel electroplating on high temperature oxidation behaviour of the FeCrAl for six hours and 100 hours.

1.5 Research scopes

The scope of this research includes:

(i) The investigation on the various electroplating techniques of nickel on FeCrAl metallic monolith.

(ii) The investigation on the modification of surface roughness and area, and the effect of ultrasonic treatment on six hours high temperature oxidation behaviour of the FeCrAl.

(iii) The investigation on nickel oxide developed as a catalyst on FeCrAl substrate using ultrasonic, nickel electroplating, and oxidation process methods.

(iv) The investigation on high temperature oxidation behaviour of FeCrAl substrate treated using ultrasonic and nickel electroplating methods at the temperature of working condition of the catalytic converter for 100-hours oxidation processes.

CHAPTER 2

LITERATURE REVIEW

This chapter presents the theoretical background and previous work by the researchers on catalytic converter components and its preparation methods. The ultrasonic treatment, nickel electroplating, and oxidation process are also highlighted.

2.1 Catalytic converter components and its preparation

A catalytic converter consists of four basic components, i.e. substrate, washcoat, catalyst, and casing (Sebayang *et al.*, 2009; Searles, 2002). Substrate, washcoat, and catalyst are the most interesting topic which usually discussed by many researchers. Therefore, these three components discussed in this chapter.

2.1.1 Substrate

Substrate is a support, on which the catalyst is deposited, and therefore, it is often called a "catalyst support". Gulati (2006) explains that the substrate is an integral part of a catalytic converter system that has a primary function to bring the maximum active catalyst. It must withstand a variety of severe operating conditions, namely rapid changes in temperature, gas pulsations from the engine, chassis vibrations, and road shocks. It supports the catalyst used in an exhaust of a combustion chamber in order to meet the demand for low pressure drop (Ersson & Järås, 2006).

In order to accommodate the catalyst in significant amounts, substrate must be provided with a high surface area. Twigg & Webster (2006) suggests that the design of substrate must provide a maximum surface area. The catalyst coating is applied on this surface area and on which the pollutant gases must impinge in order to react.

Ferritic steel (FeCrAl) is the famous metallic material for catalytic converter substrate. The FeCrAl selected as the substrate due to the high temperature oxidation resistance. Metal supported automotive catalytic converter bodies according to Nicholls & Quadakkers (2002) are based on ferritic steels with 5-8wt% aluminium, 17-22wt% chromium, plus small additions of reactive elements. These elements added to improve the oxidation resistance of the alloy and oxide adhesion. These alloys are protected by the formation of a slow growing surface oxide, usually alumina. It is critical to component life if naturally formed alumina protective layer is maintained (Klower, *et al.,* 1998).

Twigg & Webster (2006) explains that the advantage of ferritic steels lies not only in their resistance to corrosion, but when appropriately treated they have strongly adhering oxide film on their surface. This material if heated to 300-400 ^{o}C, the surface oxide film which is chromina rich developed. However, at temperatures above 800 ^{o}C an alumina-rich surface is developed, which endows the steel with excellent high temperature resistance. In distinction, austenitic steels, which also have good high-temperature resistance (Figure 2.1), develop an iron-rich surface layer which at high temperatures tends to flake off, or "spall," as shown in Figure 2.2.

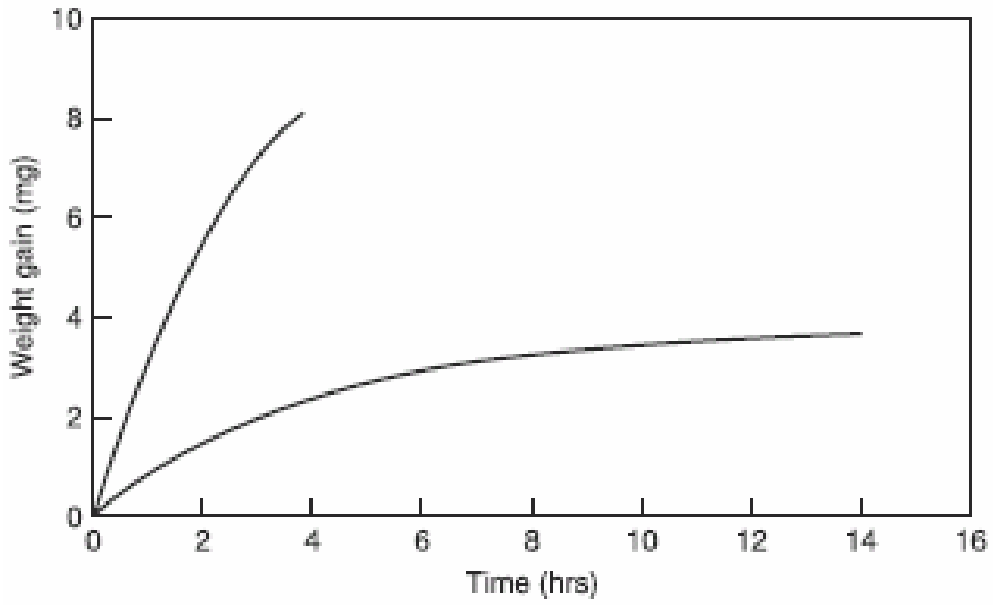
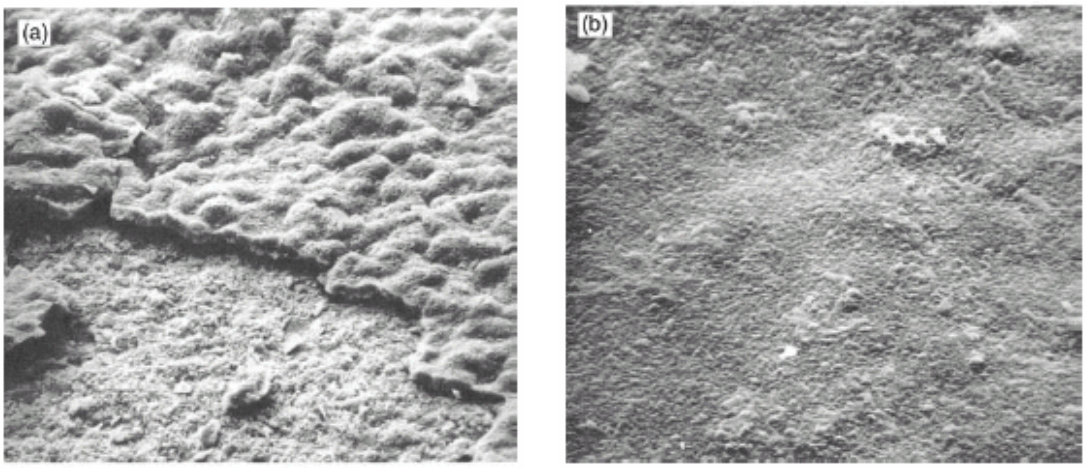


Figure 2.1: Comparison of thermo gravimetric oxidation of austenitic (upper curve) and aluminium-containing ferritic steels (lower curve) showing weight gain at 1200 ^{o}C due to surface oxidation as a function of time (Twigg & Webster, 2006)



(a) (b)

Figure 2.2: Scanning electron microscopy images showing the surface of (a) austenitic and (b) aluminium-containing ferritic steels after heat treatment in air (Twigg & Webster, 2006)

Some methods are necessary to improve the surface area for the substrate (Twigg & Webster, 2006). The previous effort on developing high surface area of metallic substrate is to conduct a simulation to obtain an optimal geometry and create

an innovative tool to produce a spiral corrugated foil with length 150 cm, width 100 cm and the thickness 0,11 mm, 0, 065 and 0, 045 mm (Sebayang *et al.,* 2009).

2.1.2 Washcoat

Washcoat is a kind of oxide material which developed on the substrate to improve adhesion of the catalyst onto the substrate. The washcoat is a thin layer of alumina (Al_2O_3) coating, typically 20-150 μm thick with a high surface area on the top of substrate. The surface of monolith support needs to be coated with a layer of high surface area material, commonly known as washcoat, in which the catalyst is dispersed (Hayes & Kolaczkowski, 1997). Heck, Farrauto, & Gulati (2002), explains that a washcoat as the catalyst's carrier. Several examples of a high surface area carrier are Al_2O_3, SiO_2, TiO_2, and SiO_2-Al_2O_3. Alumina (Al_2O_3) is one of the most applied washcoat materials (Xu & Moulijn, 2006; Heck, *et al.,* 2009). Figure 2.3 shows the scanning electron micrograph of ceramic monolith with square shaped cells that has been coated with washcoat and catalyst. Figure 2.4 illustrates a few select pores of a high surface area Al_2O_3 as the most commonly used carrier in catalysis. Figure 2.5 presents the cross section image of washcoat and catalyst on FeCrAl substrate (honeycomb).

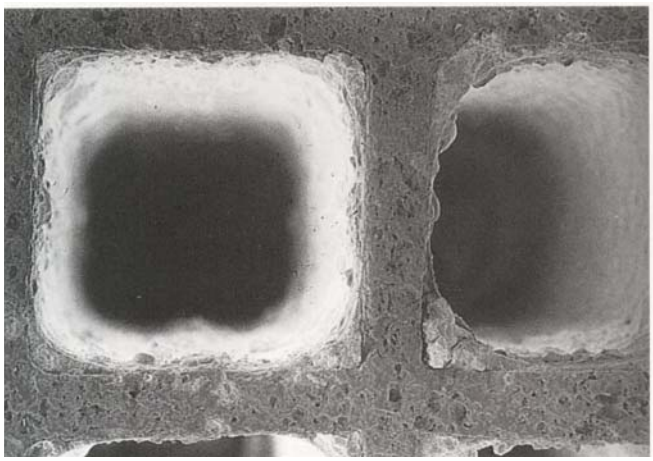


Figure 2.3: Scanning electron micrograph of a ceramic monolith with square shaped a cell that has been coated with washcoat catalyst (Hayes & Kolaczkowski, 1997)

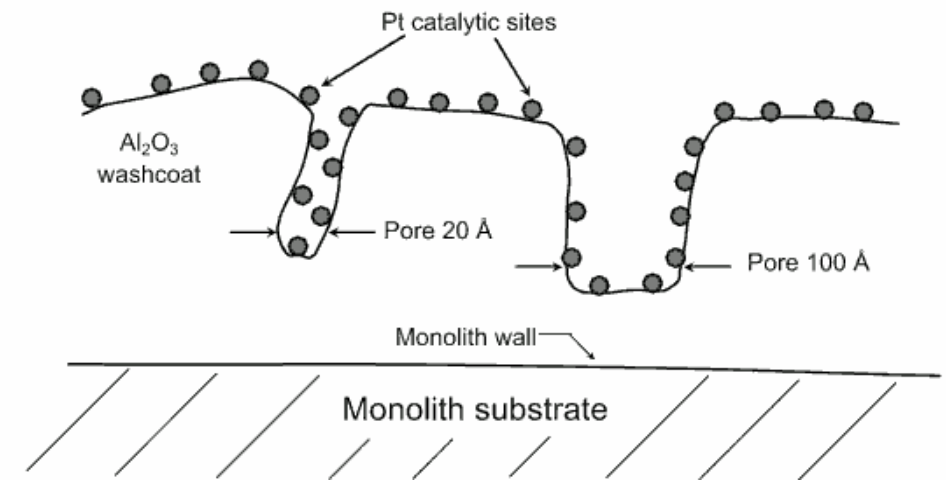


Figure 2.4: Conceptual model for catalytic sites dispersed on high surface area Al_2O_3 carrier bonded to a monolith (Heck, *et al.*, 2002)

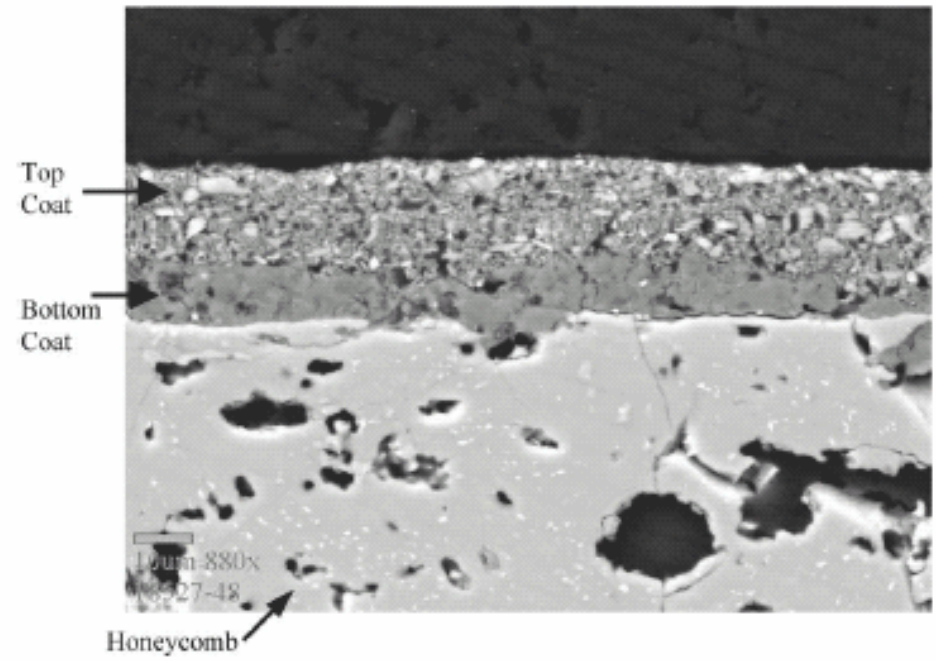


Figure 2.5: SEM image of washcoat and catalyst on FeCrAl substrate (Heck & Farrauto, 2001)

Farrauto & Bartholomew (2006) explains that catalyst carrier (supports) is porous, high surface area metal oxides or carbons having significant pore volume and capacity for preparing and reserving stable, well-dispersed catalytic phases during a reaction. This explanation supported by Ersson & Järås (2006) with an addition, that

washcoat has to remain unchanged during the extended operation of the catalyst at temperatures between 1000 and 1400 ^{o}C.

Xu & Moulijn (2006) expresses that, in principle, the surface area of monolith substrate is low. The various techniques can be used to coat an oxides layer a monolith. The alumina washcoating is the most widely used technique for monolith. The reason is that alumina has resistance to high temperature and other advantages over other oxide materials.

A study conducted by Anderson & García (2005) for a classical three way catalyst (TWC) formulation was established, using a mixture of Pt and Rh in typically 5:1 weight ratio as a precious metal catalyst, and cerium oxide as an oxygen buffer. All these ingredients were dispersed on a layer of porous alumina (the "washcoat"), possibly stabilized against sintering with appropriate additives and itself deposited on a metallic or ceramic honeycomb-type rigid structure.

A conventional washcoating technique for production catalytic monolith products generally comprise preparing a coating formed from a high surface area oxide blended with one or more catalysts and dipping the monolith structure into that coating blend (Huang & Bar-Ilan, 2002). In utilization for automotive converters the catalyst comprises one or more noble metals, such as platinum, palladium and rhodium. These noble metals are blended with high surface area metal oxides such as alumina or ceria. These washcoat are then coated upon monolithic support structures, such as ceramics honeycombs supports. Similar with Huang & Bar-Ilan (2002), Eleta *et al.* (2010) uses also washcoating technique by dipping method.

According to Zhao *et al.* (2003), the coating adhesion between the metallic support and the ceramic washcoat become a problem, so that, a widely used method to coat ceramics on metallic support is the dip coating. To compensate the intrinsic disadvantages of this method, some pre-treatment method e.g. develop a technique to grow a number of textured alumina whiskers on the surface of the metal support before dip coating and shortened the diffusion path before depositing the washcoat both of them expected greatly improved the combination ability between the alumina washcoat and the support.

The dip coating method for developing washcoat on a metallic substrate with pre-treatment method similar with Zao *et al.* (2003), was also conducted by Jia, Shen & Wang (2007). Meanwhile, the co-precipitation, sol-gel and spray-pyrolysis

methods were also applied for preparation of FeCrAlloy supported perovskite (a kind of washcoat) for catalytic combustion of methane (Yanqing *et al.*, 2010).

There are many other methods for developing washcoat and adhering catalyst, for instance, electrophoretic deposition (Sun *et al.,* 2007; Corni *et al.,* 2008), aluminizing technique (Wu *et al.,* 2005), and hydrothermal method (Wei *et al.,* 2005; Mies *et al.,* 2007; Zamaro *et al.,* 2008; Sivaiah *et al.,* 2010) and, etc. However, these existing methods were mostly complicated, in addition, usually employ material which in a form of powders.

2.1.3 Catalyst

Catalyst is a material that used to accelerate a reaction but without belonging to the reaction. Hayes & Kolaczkowski (1997) explains that catalyst is a substance which is introduced to a mixture with the intent to increase the rate of reaction. Meanwhile according to Bartholomew & Farrauto (2006), catalyst is material that enhances the rate and selectivity of a chemical reaction and in the process is cyclically regenerated. Sebayang *et al.* (2009) explains that catalyst accelerate the chemical reaction of oxidation and reduction but neither products nor reactants of the reaction.

Ersson & Järås (2006) explains that the active components in combustion catalysts are usually platinum group metals or in some case transition metal oxide. Heck, Farrauto, & Gulati (2009) argues that it was known that the precious metals, Pt and Pd, were excellent oxidation catalysts; however, the cost and supply of these materials were bothersome. Therefore, many base metal candidates were investigated, such as Cu, Cr, Ni, and Mn. They were less active than the precious metals but substantially cheaper and more readily available.

Casella *et al.* (1998), studies the preparation and characterization of different nickel catalysts for the oxyreforming reaction by impregnating two different precursor compounds (nickel nitrate and nickel acetylacetonate) into α-Al_2O_3 and α-Al_2O_3 modified by a layer of aluminum oxide. The results showed an increment in the dispersion of the active phase and to a more active catalyst.

Kis *et al.* (1998), investigates the influence of nickel oxide loading and temperature of heat treatment on the structure, texture and reducibility of co

precipitated NiO-$A1_2O_3$ catalyst. The results show that the interactions in co precipitated NiO-Al_2O_3 system are intensive.

Raney type catalysts by means of a two-step procedure: i) mechanical alloying (MA) of the metals and ii) alkaline aluminum leaching is prepared by Zeifert *et al.* (2000). It is concluded that MA is a novel alternative related to the synthesis of skeletal Ni catalysts.

Quintana-Melgoza, Gómez-Cortés & Avalos-Borja (2002) compares $NiWO_4$, NiO, and WO_3 catalysts for simultaneous conversion of NO and CO. Samples is synthesized by reacting ammonium metatungstaten and/or nickel nitrate at a high temperature (773 to 903 K) under an oxygen stream. The catalytic reduction of NO by CO takes place in the temperature range (523 to 973 K) under highly reductive conditions (NO:CO = 1:5) over $NiWO_4$, NiO, and WO_3, respectively. In the range (523 to 723 K) NiO is more active than $NiWO_4$ and WO_3 catalysts.

Xiang *et al.* (2004), develops an advanced hydrothermal modification method to synthesis Ni/Al_2O_3 catalyst with perfect activity. The experimental results indicate that the modification of the impregnation samples at elevated temperatures enhanced the absorption of $Ni(NO_3)_2.xH_2O$ on the surface of supporters which is composed mainly of $Al(OH)_3$ and AlOOH, leading to the formation of the porous sintering products ($NiAl_2O_4/Al_2O_3$) with bigger specific surface areas and higher Ni contents. The conversion of CH_4 increases a lot by using the hydrothermal-modified catalyst instead of using the catalyst prepared via the traditional impregnation–sintering route.

The use of Ni as a catalyst for the electro-oxidation of methanol in an alkaline medium is studied by cyclic voltammetry (Abdel Rahim *et al.,* 2004). Ni is dispersed on graphite by the electro-deposition from acidic $NiSO_4$ solution using potentiostatic and galvanostatic techniques. It is concluded from the electro-chemical measurements and SEM analysis that methanol oxidation starts as Ni-oxide is formed on the electrode surface.

Fonseca & Assaf (2005) prepares nickel catalysts from hydrotalcite precursors, characterizes and tests in the reaction of methane steam reforming to produce hydrogen. The precursors are synthesized by the traditional technique, with co-precipitation of Ni, Mg and Al nitrates with carbonate; coprecipitation of Mg and Al nitrates with pre-synthesized nickel chelate and anion-exchange of NO^{3-} of hydrotalcite with nickel chelate. The catalytic tests demonstrate high methane

conversion, high activity for hydrogen production and high stability during the time of reaction for a molar ratio in the feed $H_2O:CH_4 = 2:1$.

A catalyst configuration comprises: a substrate, a NiO layer was disposed on the substrate, and a catalyst layer comprising a NOx adsorbing catalyst was patented by Dou (2005). The method is making a NOx absorber by thermally treating NiO to a temperature of about a maximum catalyst application temperature minus 100 ^oC and the maximum catalyst application temperature.

Ochoa *et al.* (2007) prepares a series of hydrotalcite-like catalysts (HT) with different Ni loadings by a co-precipitation technique and compared with catalysts prepared by conventional incipient wetness impregnation. The co-precipitation route results in a stronger interaction between the support and nickel than the incipient wetness route.

Xiancai *et al.* (2008) prepares the nickel-based catalysts by the sol-gel method and used for the CH_4 reforming with CO_2. Compared with the catalyst prepared by the impregnation method, the results indicated that the catalysts prepared by the sol-gel method had larger specific surface area, showing higher catalytic activities and exhibiting perfect desorption and reduction performances.

Jang *et al.* (2008) studies the characterization of Al_2O_3 supported Ni catalysts derived from the RF non-thermal plasma technique with in-situ XRD, TPR-MS and STEM and on relating the results to the enhanced activity and stability of benzene hydrogenation. The results suggest that catalysts with plasma treatments before impregnation are relatively easier to be reduced and result in better activities under mild reduction conditions. The catalyst with a combination plasma treatment demonstrates that the effect of a combination plasma treatment is larger than either the plasma treatment before or after the impregnation alone.

Shi & Liu (2009) applies the room temperature glow discharge plasma to treat the nickel precursor supported on SiO_2. According to the catalyst characterization, the calcinations thermally of the plasma treated sample show a small particle size and high dispersion. Such prepared sample presents high conversions of carbon monoxide and hydrogen for the reaction of methanation with a significantly improved anticarbon deposition performance. The plasma-treated sample shows enhanced metal-support interaction and keeps good dispersion after reaction.

Dueso *et al.* (2010), studies the reactivity of a Ni-based oxygen carrier prepared by hot incipient wetness impregnation (HIWI) on α-Al_2O_3 with a NiO content of 18 wt%. The reaction was catalyzed by metallic Ni in the oxygen carrier and H_2 and CO acted as intermediate products of the combustion. The test showed that there was a relation between the solid conversion reached during the reduction and the relative amount of NiO and $NiAl_2O_4$ in the oxygen carrier.

Many literatures explain that waschoat and catalyst preparation always in separated process. The FeCrAl and nickel selected and used as raw material in this research due to the advantages as has explained. Due to the FeCrAl and nickel are metal, so that the alternative possible new method for adhering nickel on the FeCrAl is electroplating technique. Ultrasonic treatment can be implemented to improve the efficiency of electroplating such as in agitation process.

2.2 Nickel electroplating

Nickel electroplating is one of the electro depositions processes that employ soluble metal anodes where direct current is made to flow between two electrodes immersed in a conductive aqueous solution of nickel salts (Di Bari, 2000). The flow of direct current causes one of the electrodes (the anode) to dissolve and the other electrode (the cathode) to become covered with nickel. The nickel in solution is present in the form of divalent, positively charged ions (Ni^{++}). When current flows, the positive ions react with two electrons ($2e^-$) and are converted to metallic nickel (Ni^0) at the cathode surface. The reverse occurs at the anode where metallic nickel is dissolved to form divalent, positively charged ions, which enter the solution. The nickel ions discharged at the cathode are thus replenished by those formed at the anode. The basic electrical circuit for electroplating showed in Figure 2.6.

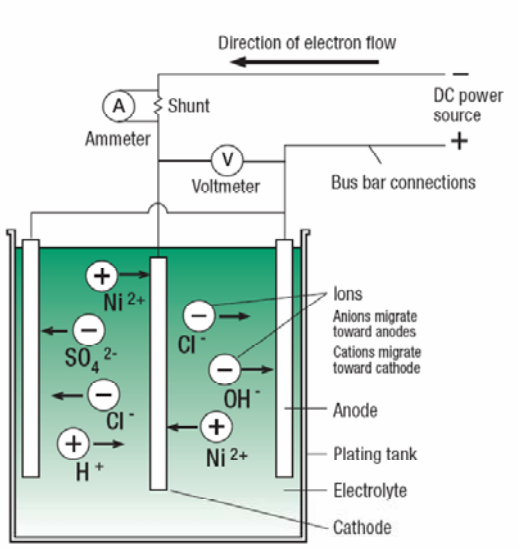


Figure 2.6: Basic electrical for electroplating (Rose & Whittington, 2002)

According to Rose & Whittington (2002), the average coating thickness can be derived by dividing the weight deposited (in grams) by the product of the density of nickel (8.907 g cm^{-3}) and the surface area to be electroplated (in dm^2) and with multiplying by 100 to obtain the thickness in micrometers (µm). Alternatively, the average thickness can be computed directly from the current and time using the following calculation:

$$T = \frac{12.294.I.t}{A} \tag{2.1}$$

where T is the average thickness (µm) and A is the area being electroplated (dm^2), I is the current that flows through the plating tank in amperes and t is the time that the current flows in hours.

The above calculation is based on 100% cathode current efficiency. The ratio of current to an area (I/A) is known as the current density**.** It will be seen that the average thickness depends on the current density and time, whereas the weight of nickel deposited (or dissolved at the anode) depends on the current and time. Usually in nickel plating, the current density will be expressed as amperes/dm^2. In practice, it will be convenient to refer to tables to estimate the ampere-hours or the current and time required to obtain a desired average thickness. The "time to electrodeposits nickel at various current densities" presented in Table 2.1.

Table 2.1: Time to electrodeposits nickel at various current densities.

Current Density (A/dm^2)	Time in Minutes to Deposit the Indicated Average Thickness of Nickel at Various Current Densities							
	5 µm	10 µm	15 µm	20 µm	25 µm	30 µm	40 µm	50 µm
1	26	51	77	100	128	154	200	255
1.5	17	34	51	68	85	102	140	170
2	13	26	39	51	65	78	100	130
2.5	11	22	32	42	53	64	84	105
3	8.5	17	26	34	43	52	68	85
4	6.5	13	20	26	33	40	51	65
5	5	10	15	20	25	30	41	50
6	4.5	8.5	13	17	22	26	34	43

Based on 95.5% cathode current efficiency

Refer to Rose & Whittington (2002) the majority of nickel plating solutions, particularly those used for decorative plating, are based on the 'Watts' formulation developed by Professor Oliver P. Watts in 1916. The Watts electrolyte combines nickel sulphate, nickel chloride and boric acid. The proportions may vary according to the application, a typical formulation together with operating parameters is given in the Table 2.2. The other nickel electroplating solutions is sulphamate nickel electroplating (Rose & Whittington, 2002). Nickel sulphamate solutions are chiefly used for the deposition of functional coatings or for electroforming. For such applications the low stress which can be achieved without the use of addition agents, the high deposition rates and desirable deposit properties offer their higher cost.

Table 2.2: Formula and operating conditions for Watts nickel electroplating solutions

Solution Component	Amount/value
Nickel Sulphate ($NiSO_4.6H_2O$)	240 - 300g/l
Nickle Chloride ($NiCl_2.6H_2O$)	30 - 90 g/l
Boric Acid (H_3BO_3)	30 - 45 g/l
Temperature	40 - 60 ^0C
pH	3.5 - 4.5
Cathode Current Density	2 - 7 A/dm^2
Deposite Rate	25 - 85 µm/hr

Some form of solution agitation and mixing is required in plating. Agitation may be by forced air, mechanical stirring, controlled flow, or sonication. Mason (2002) explains that, the effect of ultrasound has been extremely beneficial in improving the hardness of nickel deposits. Using a variety of plating solutions it has been shown that the presence of ultrasound improves the hardness of the coating with the magnitude dependent on the particular bath composition employed.

The effects of ultrasonic agitation during the electrolysis must consider cavitation phenomena-the collapse of cavitation bubbles in liquid-generated shock wave pressure, the liquid jet, and water hammer pressure (Chiba *et al.*, 2000). The physical and chemical properties of electrodeposited films are affected by pressure and flow leading to (i) increased current efficiency, rate of deposition, and limiting current density; (ii) elimination of anodic polarization; (iii) minimized or eliminated edge buildup; (iv) production of extremely uniform and well-bonded coatings; (v) reduced porosity; and (vi) reduced particle size to produce a fine-grained deposit.

A type of nickel electrolytic deposition baths using ultrasound have been developed by Chiba *et al.* (2000). The illustrations of the experimental will be presented in Figure 2.7 which shows the position of the ultrasonic vibrator and electrodes.

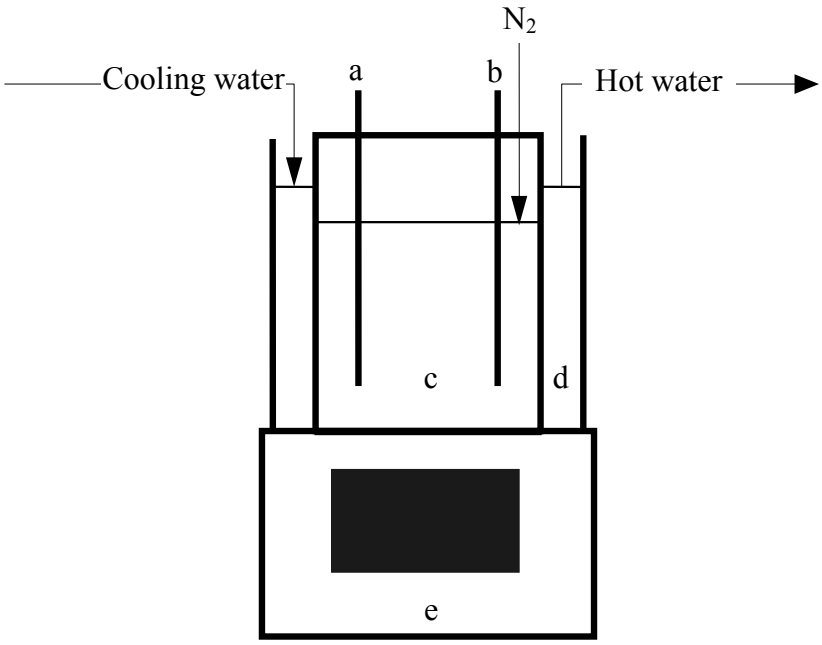


Figure 2.7: Position of electrodes and ultrasonic vibrator. (a) Cu plate; (b) Pt electrode; (c) bath; (d) cell; (e) ultrasonic source (Chiba *et al.*, 2000)

2.3 Ultrasonic treatment

In some process, the ultrasonic treatment that applied called sonication (Chiba *et al.,* 2000). However, Suslick (2001) uses high intensity sound or ultrasound to alter chemical reactions and called it sonochemistry. Mason (2002) also studies the ultrasound to chemical processes and calls it sonochemistry as well.

Ultrasound is the part of the sonic spectrum which ranges from about 20 kHz to 10 MHz and can be roughly subdivided in three main regions: low frequency, high power ultrasound (20-100 kHz), high frequency, medium power ultrasound (100 kHz - 1 MHz), and high frequency, low power ultrasound (2-10 MHz). The range from 20 kHz to around 1 MHz is used in ultrasonic treatment (Sweet, 1998).

The use of power ultrasonic to stimulate a process in liquid is currently the trend in a wide range of materials science and technology. The application of ultrasonic can used to produce and process materials that are often unobtainable by conventional process routes. The effects of ultrasonic arise from acoustic cavitations in a liquid (the formation, growth, and implosive collapse of bubbles). Ultrasonic cavitations in liquid-solid systems produce related phenomena. Cavity collapse near an extended solid surface becomes non-spherical, drives high speed jets of liquid into the surface, and creates shockwave damage to the surface (Mason, 2002). Based on this reason, ultrasonic is expected to stimulate the coating process of nickel on the FeCrAl.

The cavitation phenomenon that causes erosion on a material surface is discussed by Koivula (2000). This erosion process is as a mechanical degradation which called cavitation erosion. It can be formed when cavity implosions are violent enough, and they take place near enough to the solid material. Cavitation erosion can be identified from a specific rough mark in surfaces of component flows paths. The rough marks that resulted from cavitation on the FeCrAl substrate surface are believed useful for electroplating process.

According to Koivula (2000), it is considered that there are two possible mechanisms to cause cavitation erosion. When a cavity collapses within the body of liquid, the collapse is symmetrical. The symmetrical collapse of a cavity emits a shock wave to the surrounding liquid. When a cavity is in contact with or very close to the solid boundary, the collapse is asymmetrical. In the asymmetrical collapse, the

cavity is perturbed from the side away from the solid boundary and finally the fluid is penetrating through the cavity, and a micro-jet is formed (Figure 2.8).

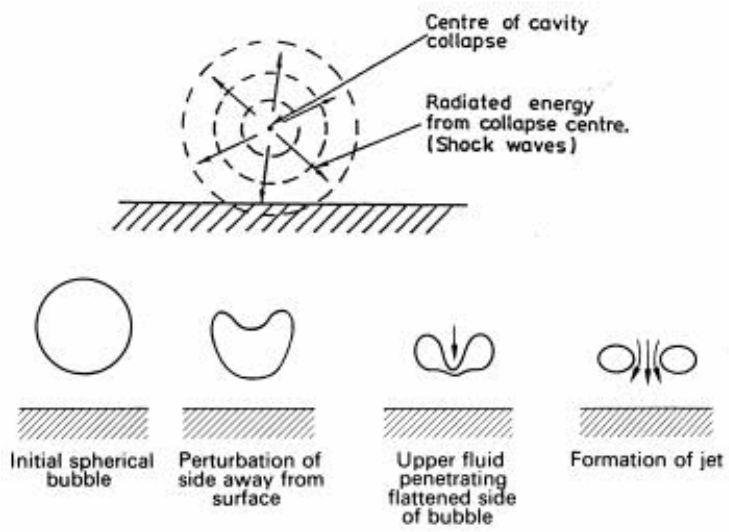


Figure 2.8: The shock-wave mechanism and micro-jet mechanism of cavitation erosion. (Koivula, 2000)

Koivula (2000) argues when a cloud of cavities collapses, the cavities do not act independently, but in concert (triggering each other's collapse). The collapse of the cavity cloud enhances the effects of the cavities adjacent to or in contact with the solid boundary. Figure 2.9 shows the example of cavitation erosion resulted from difference type of oil as the liquid that has been investigated by Koivula (2000). This explanation is the main concept that implemented in this study.

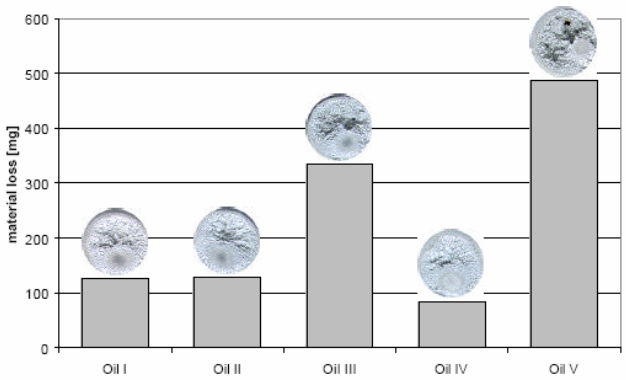


Figure 2.9: Material loss due to cavitation erosion with different oil types (Koivula, 2000)

2.4 Development of oxide layer using a high temperature oxidation process

Oxidation is an environmental phenomenon in which metals and alloys (and other materials) exposed to oxygen or oxygen-containing gases at elevated temperatures convert some or all the metallic elements into their oxides (Young, 2009). The oxide can form as a protective scale if it remains adherent, and reduces further oxidation, or may continually "spall off", exposing a fresh metal. The latter results are in progressive metal loss. The technological implications of an oxidation lie in the loss of load-bearing capability of the original metal or alloy component, eventually resulting in component failure (Bose, 2007).

Two method oxidation processes were used; there are continuous oxidation process by using a TGA and discontinuous oxidation process by using an automatic furnace with cyclic oxidation approach (Birks *et al*., 2006). Thermogravimetry is the measurement of mass change as a function of temperature or mass changes as a function of time, at a constant temperature (Khanna, 2002). Oxidation studies are usually carried out by exposing the specimen in a furnace at a fixed temperature and measuring the weight change as a function of time Badini & Laurella (2001). This is called isothermal oxidation test. Many such isothermal oxidation curves are generated at various temperatures and then utilized to determine the activation energy of the oxidation reaction. Sometimes oxidation test is carried out under cyclic conditions of temperature. In this test, the sample is exposed to a cyclic programmed, i.e. exposure for an affixed duration of time at a high temperature, followed by cooling with a specific cooling Rte: holding it for a certain time period: re-heating and holding it at a high temperature under similar conditions. Such tests are carried out for a number of cycles ranging from 10-20 to 100-200. Weight changes are measured after each cycle. Such test is known as a cyclic oxidation test and then give information about the stability of the oxide scale under such as severe oxidation condition not only of heating at a particular temperature but also under the effect of thermal stresses, generated during thermal cycles (Khanna, 2002).

The preparation of specimens in oxidation test is usually referring to ASTM G 54-84 (1996) standard. The results from oxidation test can be analyzed to obtain parabolic rate constant (k_p) follows the Wagner theory (Smallman & Bishop, 1999; Badini & Laurella, 2001). For FeCrAl specimen, the k_p value of oxidation test can be used to predict the time to failure of FeCrAl substrate (Klower *et al.*, 1998).

The Al_2O_3 layer is believed occurred on FeCrAl substrate after an oxidation test (Klower *et al.*, 1998; Badini & Laurella, 2001; Nicholls & Quadakkers, 2002; Zhao *et al.,* 2002; Twigg & Webster, 2006). It is caused by the Al element in the FeCrAl substrate. At room temperature Al is always covered with 2-3 nm amorphous alumina. At temperatures between 350 and 425 ^{o}C the amorphous film grows with parabolic kinetics, and at a temperature above 425 the kinetics are complex (Birks *et al*., 2006).

The NiO is believed can be produced from Ni by using an oxidation process. Under normal temperature and pressure condition nickel only forms one oxide, NiO (Birks *et al*., 2006). Meanwhile Wright & Andrew (1949) explain that the NiO has a possibility to be formed through the oxidation of metal (pure nickel), it overcomes the problem of powder material usage. Sato *et al.* (1998) invented that the nickel-carbon composite film on the substrate in the foregoing manner (spattering) is then heat-oxidized in an atmosphere of a gas comprising oxygen, such as air; to form the desired nickel oxide film with a heating temperature of about 400 ^{o}C will suffice. Young (2009) investigated that the significant developed NiO from Ni substrate resulted at 900 ^{o}C and above. The early measurement by (Birks *et al*., 2006) shows that the oxidation of nickel over temperature range 700 -1300 obtains a surprising variation of the parabolic rate constant over four orders of magnitude.

Nickel as a catalyst is also in a form of nickel oxide (Heck *et al*., 2009). The common nickel oxide catalyst is synthezed on a substrate directly from nickel oxide powders. In this work, due to the nickel has coated on the FeCrAl substrate it is possible to create nickel oxide by heating on elevated temperature. The elevated temperature is also possible to develop an alumina layer on the FeCrAl substrate that needed as washcoat. So that, as a part to understand the oxidation process this sub chapter discusses about a high temperature oxidation process related to the development of oxide layer.

CHAPTER 3

METHODOLOGY

This chapter describes the steps of the research to obtain the best result for preparation of NiO catalyst on FeCrAl substrate for catalytic converter application. The approach was started with assessment of FeCrAl treated using various nickel electroplating process based on the weight gain during oxidation, then short term oxidation, and the last is long term oxidation. The steps are summarized as a flowchart in Figure 3.1. The materials and experimental procedures that consist of an electroplating, ultrasonic treatment, oxidation process, and characterization are also described.

3.1 Materials

The materials utilized in this research were: i) FeCrAl foils (strip) (Aluchrom Yhf) supplied by ThyssenKrupp. VDM, Germany. The chemical component of Aluchrom Yhf presented in Table. 3.1. ii) Al_2O_3 powder product of Merck, Germany. iii) SiC powder supplied by Syarikat Saintifik Bersatu, Malaysia. iv) Nickel plate (pure nickel) was supplied by Centre for Technology of Nuclear Industry Materials, National Nuclear Energy Agency (BATAN) Indonesia. The general properties of nickel is presented in Table. 3.2. v) Electrolyte solutions; nickel sulphamate type. The composition of this solution is summarized in Table. 3.3.

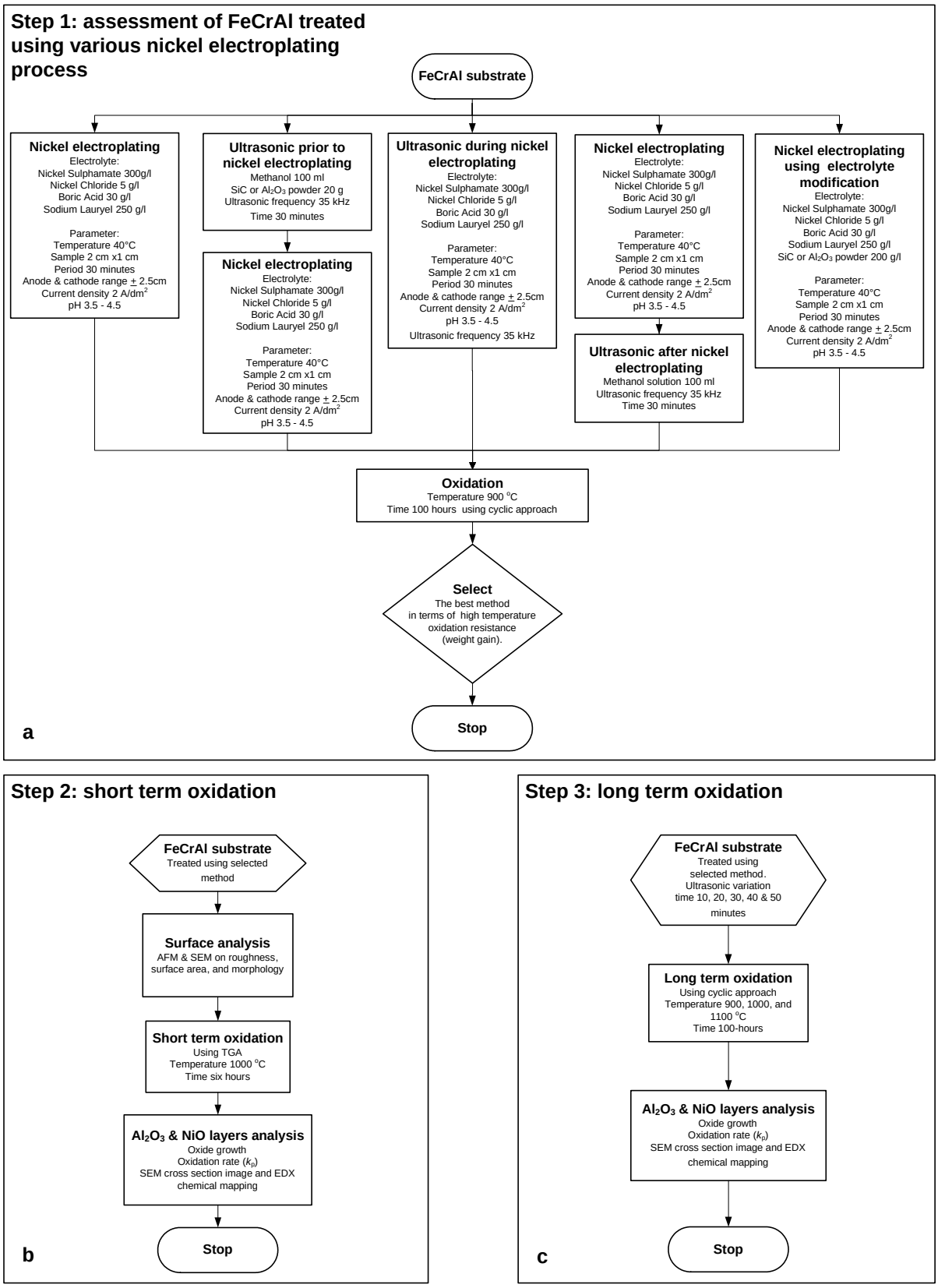


Figure 3.1: Flow chart of the research, a) assessment of FeCrAl treated using various nickel electroplating, b) short term oxidation, c) long term oxidation

Table 3.1: Chemical compositions Aluchrom Yhf (wt-%) (ThyssenKrupp, 2008)

	Ni	Cr	Fe	C	Mn	Si	Al	Zr	Y	Hf	N
min	-	19.0	bal	-	-	-	5.5	-	-	-	-
max	0.3	22.0		0.05	0.50	0.50	6.5	0.07	0.10	0.10	0.01

Table 3.2: General properties of nickel

Properties	Type/value
Element Categories	Transition Metals
Group, Period, Block	10, 4, d
Density(gcm^{-1})	8.9 g.cm^{-3} at 20°C
Melting Point (^oC)	1455
Crystal Structure	FCC
Ionic Radius (pm)	0.069 nm (+2) ; 0.06 nm (+3)
Thermal Conductivity (300K)($Wm^{-1}K^{-1}$)	90.9

Table 3.3: Electrolyte solution compositions

Solution Component	Amount/value
Nickel Sulphamate [$Ni(NH_2SO_3)_2.4H_2O$)]	300g/l
Nickel Chloride ($NiCl=.6H_2O$)	5 g/l
Boric Acid (H_3BO_3)	30 g/l
Sodium Lauryel	250 g/l
Temperature	40 ^oC
pH	3.5 - 4.5

3.2 First step: assessment of FeCrAl treated using various nickel electroplating process

In this work, the various nickel electroplating process on the FeCrAl were conducted as the preliminary study to obtain the best method to adhere nickel on the FeCrAl substrate. The study analyzed the influence of various nickel electroplating processes on the FeCrAl metallic monolith for high temperature oxidation resistance. The proposed new ideas to adhere nickel as a catalyst on the FeCrAl substrate are divided into five methods as follows:

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